



## INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification <sup>6</sup> : C30B 11/00, 11/12, 29/40		A1	(11) International Publication Number: <b>WO 97/13891</b>
			(43) International Publication Date: 17 April 1997 (17.04.97)
(21) International Application Number: PCT/PL96/00017 (22) International Filing Date: 11 October 1996 (11.10.96) (30) Priority Data: P.310929                      13 October 1995 (13.10.95)                      PL (71) Applicant (for all designated States except US): CENTRUM BADAŃ WYSOKOCIŚNIENIOWYCH [PL/PL]; Polskiej Academii Nauk, ul. Sokolowska 29/37, PL-01-142 Warszawa (PL). (72) Inventors; and (75) Inventors/Applicants (for US only): BARANOWSKI, Jacek, M. [PL/PL]; ul. Zwm 22 m.16, PL-02-786 Warszawa (PL). BOCKOWSKI, Michał [PL/PL]; ul. Klaudyny 32 m.313, PL-01-684 Warszawa (PL). GRZEGORY, Izabella [PL/PL]; ul. Nałkowskiej 9 m.10, PL-01-886 Warszawa (PL). JUN, Jan [PL/PL]; ul. Klaudyny 18 m.175, PL-01-684 Warszawa (PL). KORONA, Piotr, Krzysztof [PL/PL]; ul. Pachnacza 83 m.40, PL-02-790 Warszawa (PL). KRUKOWSKI, Sta- nisław [PL/PL]; ul. Zaranie 8, PL-02-400 Warszawa (PL). PAKUŁA, Krzysztof [PL/PL]; ul. Orzycka 16 m.46, PL- 02-695 Warszawa (PL). POROWSKI, Sylwester [PL/PL]; ul. Wieniawskiego 5 m.7, PL-01-572 Warszawa (PL). STĘPNIEWSKI, Roman [PL/PL]; ul. Doroszewskiego		7 m.24, PL-01-318 Warszawa (PL). WRÓBLEWSKI, Mirosław [PL/PL]; ul. Nowolipie 26 m.85, PL-01-011 Warszawa (PL). WYSMOŁEK, Andrzej [PL/PL]; ul. Smyczkowa 9 m.201E, PL-02-678 Warszawa (PL). (81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IL, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG). Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	
(54) Title: METHOD OF MANUFACTURING EPITAXIAL LAYERS OF GaN OR Ga(Al,In)N ON SINGLE CRYSTAL GaN AND MIXED Ga(Al,In)N SUBSTRATES			
(57) Abstract			
<p>A method of manufacturing epitaxial layers of GaN or mixed Ga(Al,In)N on single crystal substrates of GaN or Ga(Al,In)N using known methods of epitaxial growth from the liquid or vapor phase, where the substrates are plate-like single crystals of GaN or Ga(Al,In)N obtained by the crystallization of the first layer of the substrate from supersaturated nitrogen solution in gallium or GaAlIn solution in the temperature range, <math>T_1</math>, of 600-2000 °C, under high pressure of pure nitrogen or nitrogen containing gas mixture. Thereafter the method includes crystallization of a second or epitaxial layer on the substrate at a temperature <math>T_2</math> not higher than <math>T_1</math> after decreasing the gas pressure by at least of 200 bar until the second layer attains the prescribed thickness. The epitaxial layer is formed on the first layer by Metal Organic Chemical Vapor Deposition (MOCVD) or Molecular Beam Epitaxy (MB) and is characterized by a smooth gallium surface on a first side and rough nitrogen surface on a second side upon which the epitaxial growth is effected by the known methods.</p>			

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# **METHOD OF MANUFACTURING EPITAXIAL LAYERS OF GaN OR Ga(Al, In)N ON SINGLE CRYSTAL GaN AND MIXED Ga(Al,In)N SUBSTRATES**

## **Field of the Invention**

This invention relates to a method of manufacturing of epitaxial layers, and in particular to a method of manufacturing epitaxial layers of pure GaN or mixed Ga(Al,In) composition on a substrate of single crystal of either GaN or Ga(Al, In)N.

## **Background of the Invention**

At present, the method of fabrication of epitaxial layers of Ga(Al,In)N is known, in which  $\text{Al}_2\text{O}_3$ , SiC or other single crystals are used as substrates. The layers are deposited by Metal Organic Chemical Vapor Deposition (MOCVD) method which employs trimethylgallium  $(\text{CH}_3)_3\text{Ga}$ ,

trimethylaluminum  $(\text{CH}_3)_3\text{Al}$  or trimethylindium  $(\text{CH}_3)_3\text{In}$  as transport agents for metal atoms and ammonia as a transport agent for the atoms of nitrogen. Hydrogen, nitrogen or their mixture is used as a carrier gas. A typical ratio of the reactants, i.e.  $\text{NH}_3$  to  $(\text{CH}_3)_3\text{Ga}$ ,  $(\text{CH}_3)_3\text{Al}$  and  $(\text{CH}_3)_3\text{In}$ , is in the proximity of 8000:1. In the region of the layer-substrate junction, other buffer layers of GaN or AlN are deposited in the temperatures much lower than that of the main layer in order to reduce the lattice strain. The buffer layers of GaN are deposited in temperatures of about  $550^\circ\text{C}$  and those of AlN in the temperatures close to  $700^\circ\text{C}$ . The buffer layers are usually 50 nm thick and are either amorphous or polycrystalline. When the deposition of the buffer layer is finished, the temperature is raised and the main layer is deposited. The typical temperature of the deposition of the main layers of GaN are close to  $1025^\circ\text{C}$ . For the layers and crystals of mixed GaIn composition, these temperatures are slightly higher than those used for pure GaN and the temperatures of the deposition of layers and crystals of mixed GaInN composition are slightly lower with the deviation depending on the percentage of In and Al.

Due to the lattice misfit and the difference of thermal expansion between the substrate and the layer, the epitaxial layers and crystals obtained in accordance with the above described method may have high densities of dislocation and other lattice defects, deteriorating their electrical and optical properties.

### **Objects and Summary of the Invention**

The present invention is directed to a method of manufacturing epitaxial layers and crystals of mixed Ga(Al,In)N composition on the substrate of single pure GaN or mixed composition Ga(Al,In)N. According to the invention, a

plate-like single crystals of GaN or Ga(Al,In)N are obtained by the growth of a first layer of the substrate from the supersaturated solution of nitrogen in gallium or Ga(Al,In), preferably in the temperature range, T1, between approximately 600<sup>0</sup>C and 2000<sup>0</sup>C, under high pressure of a nitrogen or the nitrogen containing gas mixture, for approximately at least one hour. Subsequently, the pressure is lowered by at least approximately 200 bar and crystallization of a second layer of the substrate is grown at a second temperature, T2, not higher than first temperature, T1, until the prescribed thickness of the layer is attained. The second layer has a smooth surface on the so called gallium side of the substrate, and rough surface on the so called nitrogen side of the substrate. The epitaxial layers are usually grown on the so-called nitrogen side of the substrate using known methods such Molecular Beam Epitaxy (MBE), Metal Organic Chemical Vapor Deposition (MOCVD), or other similar methods.

An additional aspect of the present invention is the growth of the layers or crystals on single crystals of GaN, or on Ga(Al,In)N which has been previously cut perpendicularly to c-axis on the second or nitrogen side and polished. The epitaxial layers or crystals of Ga(Al,In)N are deposited at a temperature between about 750 C and 1200 C under pressure in the range 5 mbar to 2 bar using MOCVD or other known methods. In the temperature range from approximately about 500-900<sup>0</sup>C, Molecular Beam Epitaxy (MBE) may be used as well, as other related methods.

It is therefore a general object of the present invention to provide a method of manufacturing epitaxial layers of GaN or Ga(Al,In)N on single crystal GaN and mixed Ga(Al,In) substrates.

It is another aspect of the invention to provide a method of manufacturing high quality epitaxial layers of GaN or Ga(Al,In)N on single crystal GaN and mixed Ga(Al,In) substrates applicable for use in the fabrication of optoelectronic devices.

**Brief Description of the Drawings**

FIG. 1-10 illustrates the simplified design of the high pressure apparatus for growth of the nitride crystals according one embodiment of the present invention;

FIG. 2-10 is a schematic illustration of epitaxial growth apparatus according to one embodiment of the present invention;

FIG. 3-10 illustrates a transverse sectional view of the single plate-like GaN or mixed Ga(Al,In)N crystal, obtained by growth from supersaturated nitrogen solution in gallium or GaAlIn solution in the temperature range 600-2000°C under high pressure of nitrogen or nitrogen containing gas mixture;

FIG. 4a-10 illustrates a transverse sectional view of the plate as illustrated in FIG. 3-10 and shown as grown having a smooth surface and a rough surface;

FIG. 4b-10 illustrates a transverse sectional view of the plate as in FIG. 4a-10 after polishing of the nitrogen surface.

FIG. 5-10 demonstrates the way of the cut of the substrate from single crystal;

FIG. 6-10 shows the photoluminescence spectrum in the exciton region;

FIG. 7-10 illustrates a comparison between high energy parts of the spectra of the photoluminescence and optical reflection;

FIG. 8-10 shows the change of the reflection spectrum for various temperatures;

FIG. 9-10 illustrates the dependence of the energy of free exciton

versus temperature;

FIG. 10-10 shows temperature dependence of the photoluminescence spectra.

### **Detailed Description of the Invention**

The present invention may be described with reference to three exemplary methods set forth hereinafter. It is to be noted that the scope of the invention is not limited to the three examples and that other methods within the scope of the invention may be utilized to yield the desired product.

#### **Example 1**

FIG. 1-10 illustrates a multilayer high pressure chamber 10 for fabricating epitaxial layers of GaN and mixed Ga(Al,In)N crystal on a substrate of single crystal GaN or mixed crystal Ga(Al,In)N according to the present invention. A single piece or sample 26 of metallic gallium, Ga, is placed in a crucible 12 having upper end 13 and lower end 15, and which is made of hexagonal boron nitride (BN) ceramic which is highly resistant to high temperatures and aggressive chemical environments. Crucible 12 is placed in the three-zone furnace 14 designed for work at high gas pressures and which allows for the independent control of three temperatures. Furnace 14 is located inside multilayer chamber 10, which is evacuated to a high vacuum via output 24, and subsequently nitrogen gas is pumped in via input 22 until a pressure equal to 10 kbar is attained. Furnace 14 consists of three temperature zones 16, 18, and 20, each zone including a heating spiral which is supplied with electric currents of different values.

The temperature control system operating through the heating spirals in zones 16, 18 and 20 set the temperature  $T_g$  of zone 18 equal to about

1410<sup>0</sup> C and the temperature  $T_d$  of zone 16 equal to about 1350<sup>0</sup>C. Furnace 14 with crucible 12 is then placed in high pressure chamber 10. Crucible 12 is placed near zone 16 with temperature  $T_d$ , and zone 18 with higher temperature  $T_g$ , such that furnace 14 causes a temperature gradient in gallium sample 26.

Chamber 10 is then filled with nitrogen gas or a gas mixture containing a percentage of nitrogen, thus exposing gallium sample 26 to a pressure of nitrogen or partial nitrogen pressure. Temperatures  $T_d$  and  $T_g$  are both above the melting point of gallium, and the nitrogen pressure is controlled such that the gallium sample 26 remains in the form of a liquid solution. Since the temperature  $T_g$  in zone 18 is lower than the temperature of stable gallium for a given nitrogen pressure, such as 10 kbar, a surface reaction occurs which leads to the creation of a GaN polycrystalline layer in the region of zone 18. As a result, the contact between liquid Ga and nitrogen is terminated. The temperature difference between zone 16 and zone 18 leads to different solubilities and concentrations of nitrogen in the liquid Ga, which in turn, lead to transport of the nitrogen from zone 16 to zone 18. As a result, the nitrogen concentration in zone 16 is higher than the equilibrium concentration at the lower end 15 of crucible 12 which is at a temperature of approximately 1350<sup>0</sup>C, leading to the supersaturation of nitrogen solution in the liquid gallium. Consequently, a bulk crystal 28 of GaN substrate grows and forms the first layer of the substrate.

In the subsequent stage, i.e, the stage of epitaxial growth of the crystalline layer, the pressure of nitrogen is advantageously decreased by about 1000 bar. The equilibrium temperature at this pressure is, therefore, lower than the temperature at zone 18 and is higher than the temperature of the GaN stability. The GaN surface crystalline layer then decomposes in zone 18 and the nitrogen concentration decreases. It is noted that the nitrogen concentration in zone 18 depends on the gas pressure. Consequently, the supersaturation in zone 16 can accordingly be controlled by the change of the gas pressure. This allows for the

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reduction of the supersaturation in the growth zone and reduction of the growth rate as well as additional control over the properties of the new layer. In particular the structure of the grown layer is considerably improved in this stage.

In one embodiment in accordance with the present invention, the nitrogen pressure is lowered by about 1000 bar for about one hour. During that one hour, the thickness of the layer increases by approximately  $10^{-3}$  mm. The width of the Bragg peak of x-ray diffraction on the first layer which was grown at a faster rate is equal to approximately 28-32 arc sec, whereas for the second layer with the slower growth, the Bragg peak of x-ray diffraction for the same structure is equal to 20-24 arc sec.

As illustrated in FIG. 3-10, the GaN crystal 28 obtained in this process has a plate-like shape, with two dominant surfaces perpendicular to the c-axis of the crystal lattice. The first surface 30 is a smooth, so called gallium side, and the opposite surface 32 is rough, so called nitrogen side which consists of pyramids, ridges and ribs.

After etching in aqua regia, the substrate is transferred to an MOCVD reactor. The reactor, which is schematically illustrated in FIG. 2-10, comprises chamber 100, gas containers 110, 112 for ammonia ( $\text{NH}_3$ ) and trimethylgallium (TMG), respectively, and pressure gauge 114, and flow mass controllers 116. A subsequent epitaxial layer is deposited on the rough side 32 at a temperature of approximately  $1000^\circ\text{C}$ , using hydrogen,  $\text{H}_2$ , as a carrier gas and with the reactant ratio of  $\text{NH}_3$  to TMG of approximately 8000:1.

After approximately one hour, the grown epitaxial layer, has crystallographic qualities comparable to that of the underlying substrate with a density of the dislocation of approximately  $10^{-5} \text{ cm}^{-2}$ , and with extremely narrow photoluminescence peaks. As illustrated in FIG. 9-10, the reflection spectrum has three different dispersion lines related to free exciton energies:  $E_a = 3.4761 \text{ eV}$ ,  $E_b = 3.4812 \text{ eV}$  and  $E_c = 3.499 \text{ eV}$ . These energy values are related to the absence of

the stress in the epitaxial layer. A comparison of the photoluminescence and the reflection spectra allows for the identification of the free exciton lines in the photoluminescence spectrum. The presence of free exciton lines is an indication of the remarkable quality of this grown epitaxial layer in accordance with one embodiment of the present invention.

FIG. 8-10 illustrates the change of the reflection spectra related to free excitons which can be observed in the temperature range 4.2 - 390 K. The temperature range of 4.2 - 390 K as illustrated in FIG. 8-10 characterizes a substantially wide temperature range of free exciton lines, which is an additional indication of the quality of the grown layer. The dependence of the energy of the exciton on the temperature, presented in FIG. 9-10, can be expressed as:

$$E = E_0 - \frac{0.0081 T^2}{T + 2300}$$

where  $E_0$  is the exciton energy extrapolated to a temperature equal to 0 K. The excitonic part of the photoluminescence spectrum at temperature 4.2 K is seen in FIG. 6-10.

The temperature dependence of the photoluminescence spectrum is presented in FIG. 10-10, where it can be seen that the 3.4646 eV line and the low energy structure disappears for the temperatures higher than 40K. On the contrary, high energy intensity grows. For the temperature range of 70 - 100K, this line decreases dramatically as shown by line B in FIG. 7-10. The low energy part of the photoluminescence spectrum consists of narrow line of the energy at about 3.4646eV and rectangular band in the range of about 3.454 - 3.464 eV. Despite the fact that this part is the most distant from the free exciton energy, the temperature dependence suggests that it has the lowest activation energy. This part of the spectrum has not been observed in the past, but is now observed for the layers obtained according to the method of the present invention.

### Example 2

A single piece or sample 26 of metallic gallium is placed in crucible 12 as illustrated in FIG. 1-10, and undergoes the method of the growth described hereinabove in the Example 1 until a crystal is obtained having the form of a platelet dimensions of approximately 0.5 mm x 2 mm x 2 mm. The width of the Bragg peak of this crystal is approximately 28-35 arc sec. The crystal has two surfaces, perpendicular to the c-axis of the crystal lattice; the gallium side 30, which is substantially smooth, and the nitrogen side 32, which is substantially rough and consists of pyramids, ridges, a ribs, as illustrated in FIG. 4a-10. The crystal platelet is subsequently polished until it is optically smooth, as shown in FIG. 4b-10. It is then etched in aqua regia and subsequently inserted into an MOCVD reactor (shown in FIG. 2-10). A layer of Ga(Al,In)N is deposited on the rough nitrogen side 32 at a deposition temperature of approximately 1000<sup>0</sup>C, and with a reactant ratio of NH<sub>3</sub> to TMG of approximately 8000:1, with hydrogen used as a carrier gas.

After approximately one hour, the obtained layer has crystallographic qualities close to the substrate, with a dislocation density below 10<sup>5</sup> cm<sup>-2</sup>. The photoluminescence lines are extremely narrow. The main peak related to the bound exciton has width smaller than 1 meV. This width is substantially smaller than that which has been reported in the prior art to date.

### Example 3

A single piece or sample of metallic gallium 26 is placed in the crucible 12 as illustrated in FIG.1-10, and undergoes the method of growth described hereinabove in Example 1. Over a period of 50 hours a GaN single crystal is obtained having dimensions of approximately 8 mm x 4 mm. The

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obtained GaN crystal has a polyhedral shape corresponding to the main crystallographic axes of the wurtzite structure. One of the surfaces of the crystal is the nitrogen side 32 as illustrated in FIG. 4a-10, and is perpendicular to the c-axis of the crystal lattice. The GaN crystal is then cut at 33 as illustrated in FIG. 5-10, into small plates or wafers perpendicular to the c-axis of the crystal lattice. Subsequently these plates or wafers are polished on the nitrogen side 32, and the layers are then deposited on each of the plates using the method described hereinabove in Example 2.

Thus, while there have been shown and described and pointed out fundamental novel features of the invention as applied to preferred embodiments thereof, it will be understood that various omissions and substitutions and changes in the form and details of the disclosed invention may be made by those skilled in the art without departing from the spirit of the invention. It is the intention, therefore, to be limited only as indicated by the scope of the claims appended hereto. It is to be understood that the drawings are not necessarily drawn to scale, but that they are merely conceptual in nature.

## Claims:

1. A method of depositing an epitaxial layer of pure GaN or mixed Ga(Al,In)N on a substrate selected from the group consisting of GaN or mixed Ga(Al,In)N in the vapor or liquid phase, the method comprising the steps of:

forming a substrate of single crystals selected from the group consisting of GaN or Ga(Al, In)N, from a supersaturated solution of nitrogen in a liquid selected from the group consisting of Ga, Al or In, wherein said supersaturated solution has a temperature in the range of about 600-2000 C, and wherein said substrate forms under a high pressure nitrogen or nitrogen containing gas, said substrate having a first side and a second side, said first side being a gallium side and having a smooth surface, said second side being a nitrogen side and having a rough surface; and

growing an epitaxial layer of a material selected from the group consisting of GaN or Ga(Al, In)N on said nitrogen side of said substrate.

2. The method according to claim 1, further comprising the step of polishing said rough surface of said nitrogen side of said substrate before growing said epitaxial layer on said nitrogen side.

3. The method according to claims 1, wherein prior to said growing step, the method further comprises the step of cutting from said substrate a wafer perpendicular to the crystallographic c-axis and polishing said nitrogen side of said wafer.

4. The method according to claims 1, 2, and 3 in which said step of growing said epitaxial layer is effected by Metal Organic Chemical Vapor Deposition (MOCVD) at a temperature in the range of about 750-1200<sup>0</sup>C under a pressure not lower than about 5 mbar and not higher than 2 bar.

5. The method according to claims 1, 2 and 3, in which the step of growing said epitaxial layer is effected by Molecular Beam Epitaxy (MBE) in the temperature range between 500-900<sup>0</sup>C.

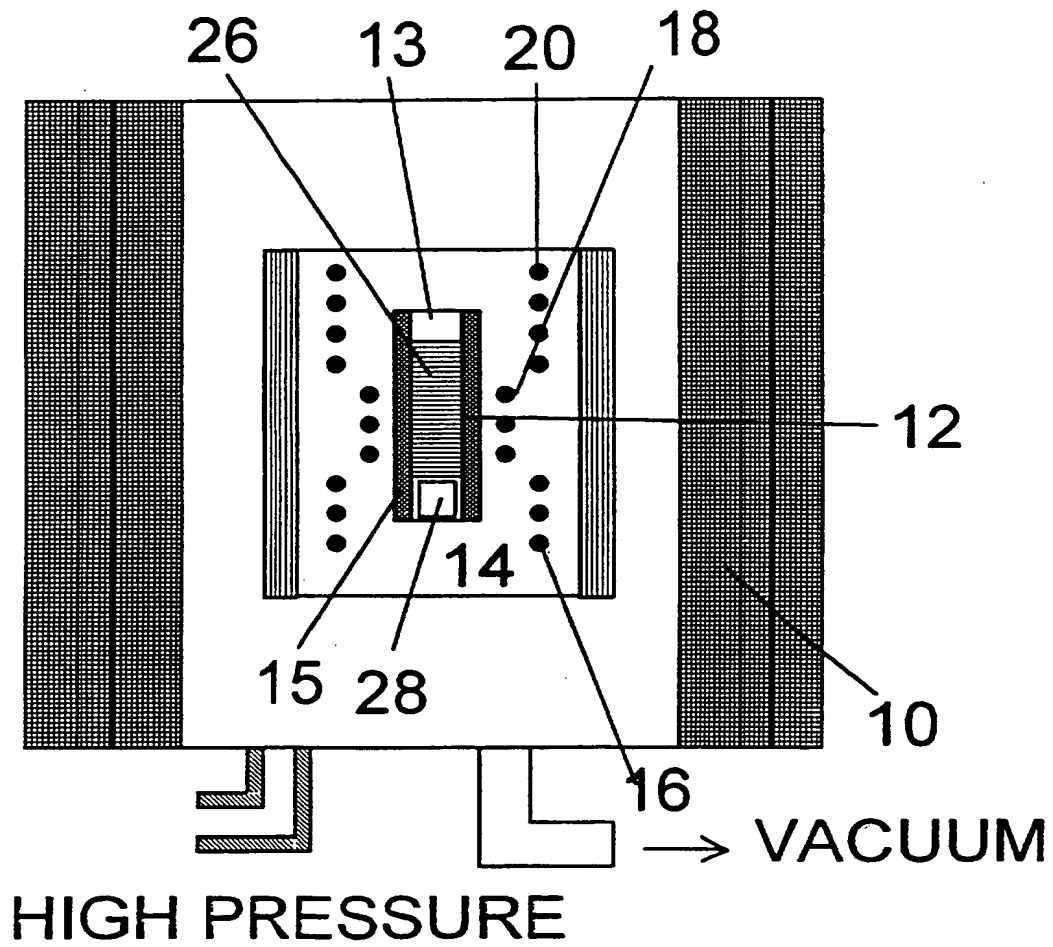


Fig 1.

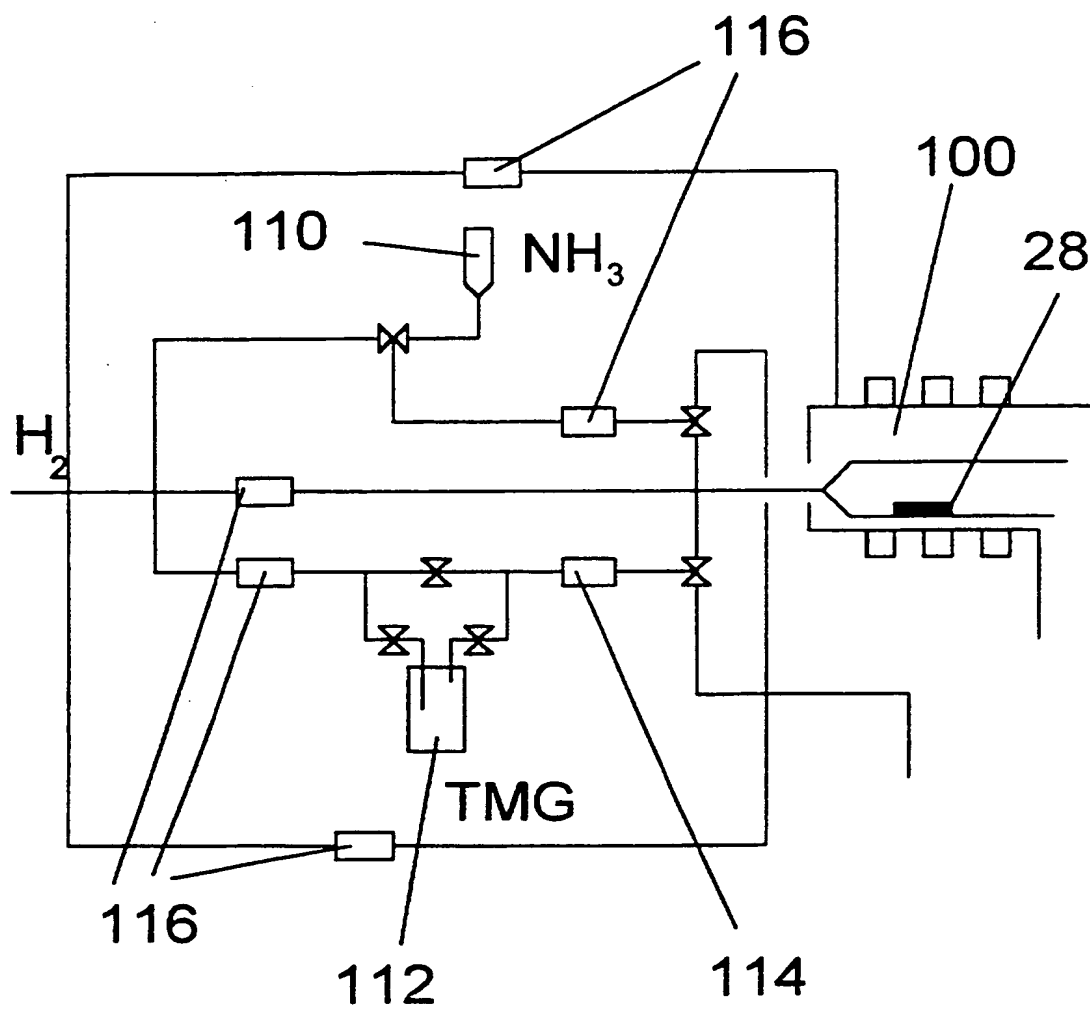


Fig 2

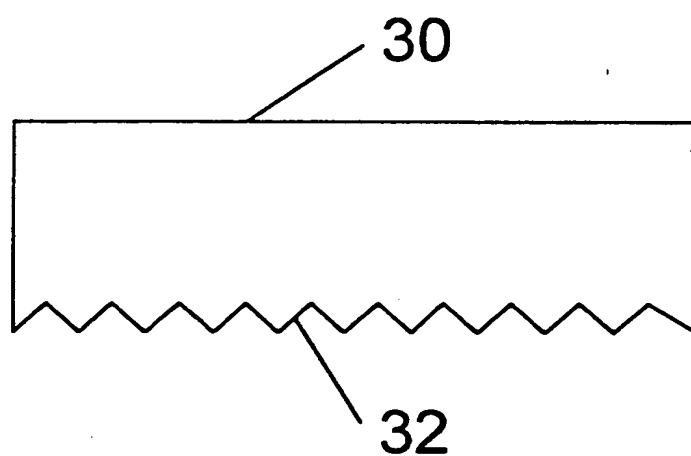


Fig 3.



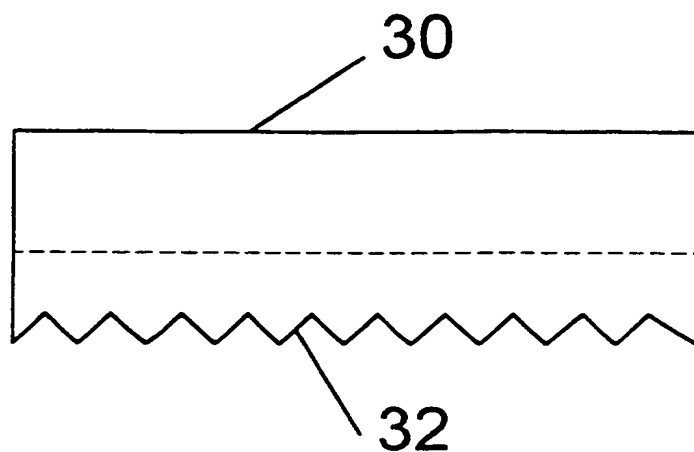


Fig 4a-

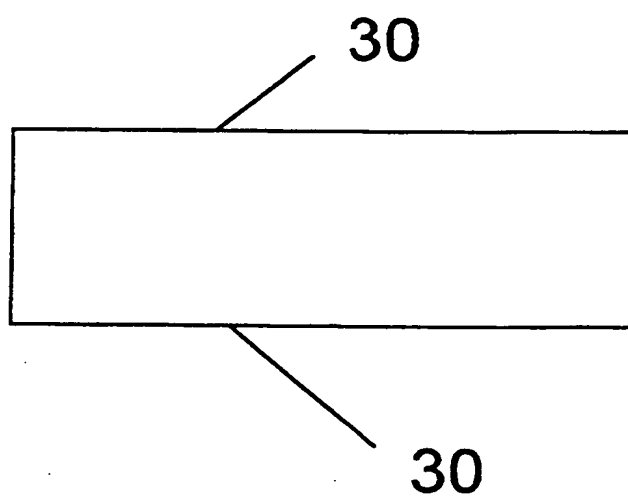


Fig 4b

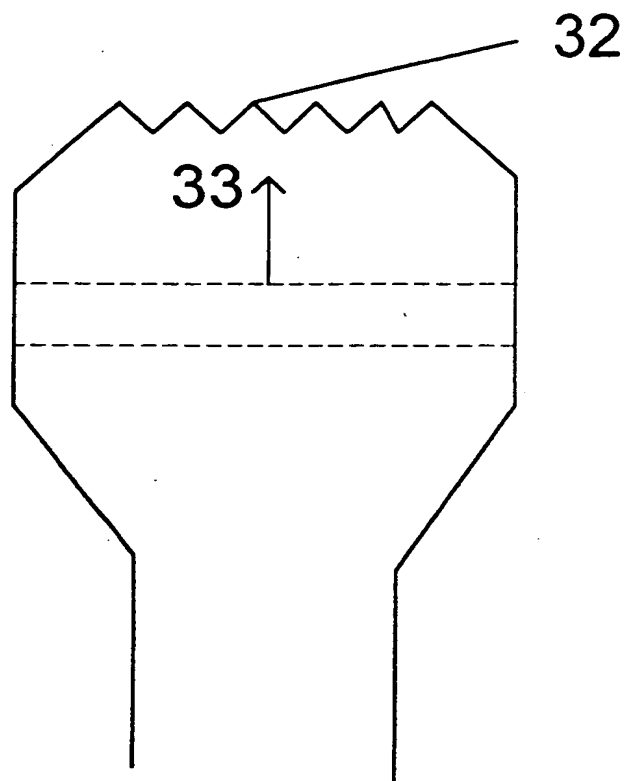


Fig 5.

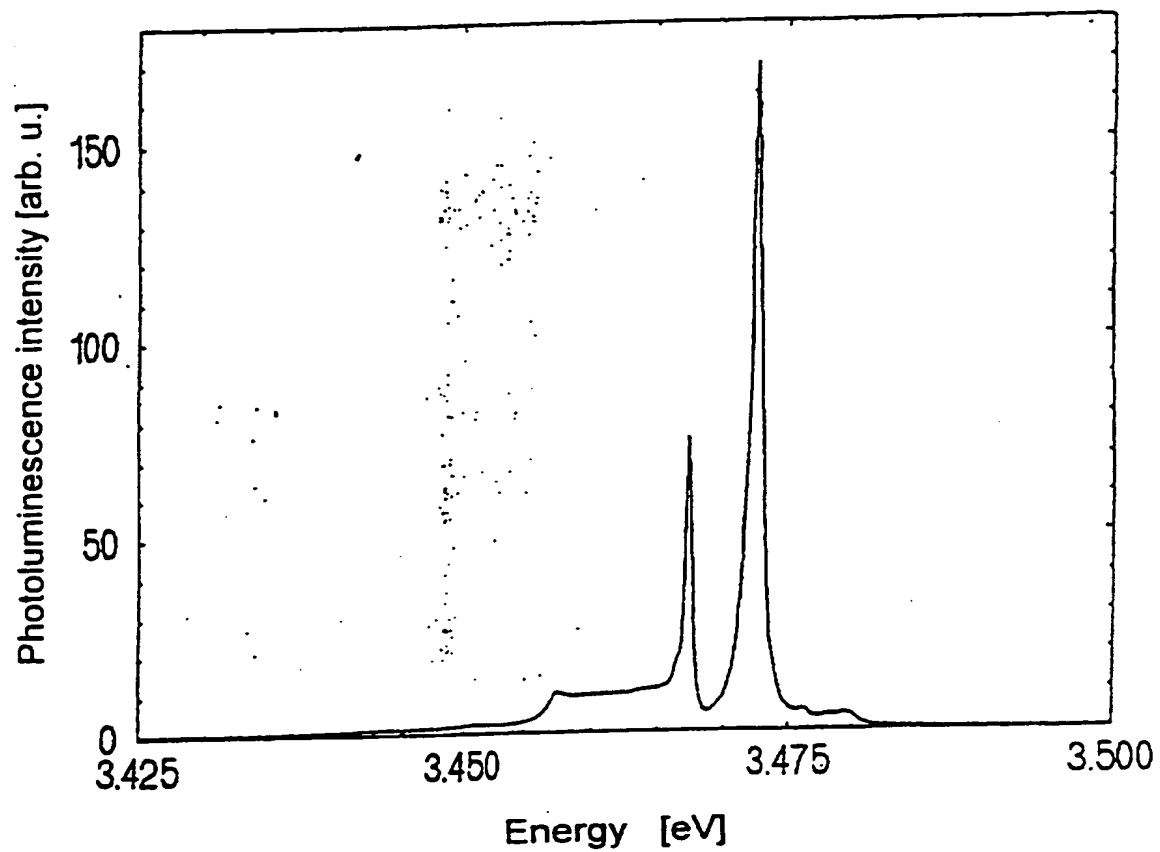


Fig 6

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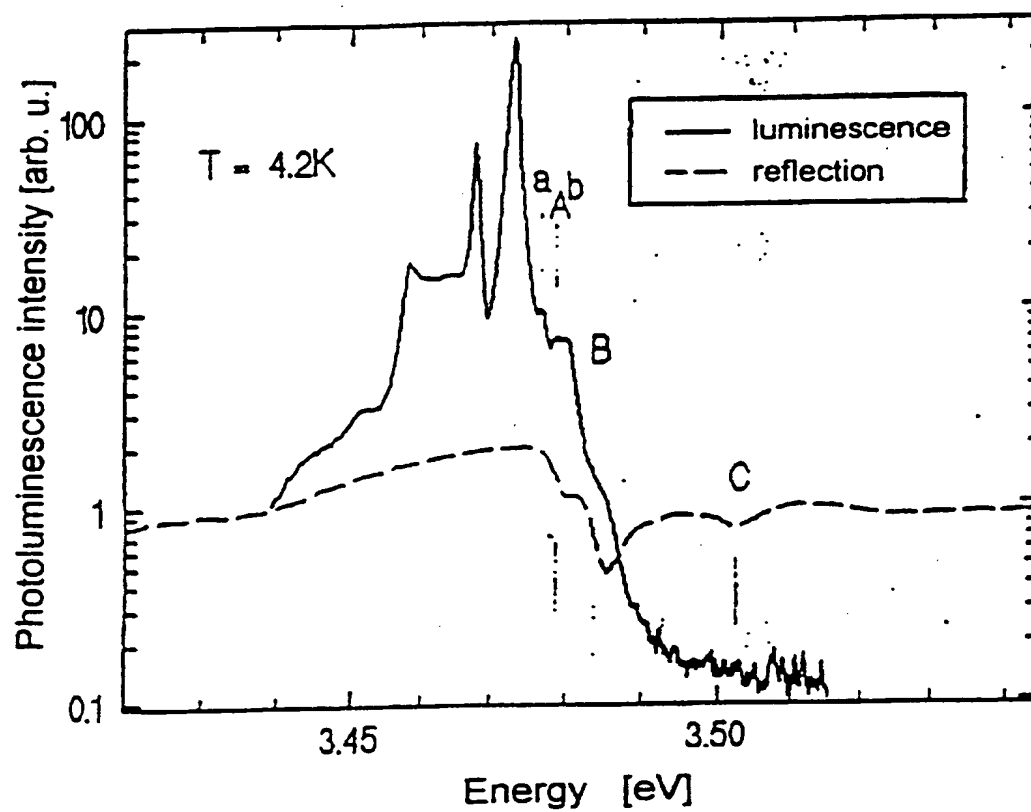


Fig 7

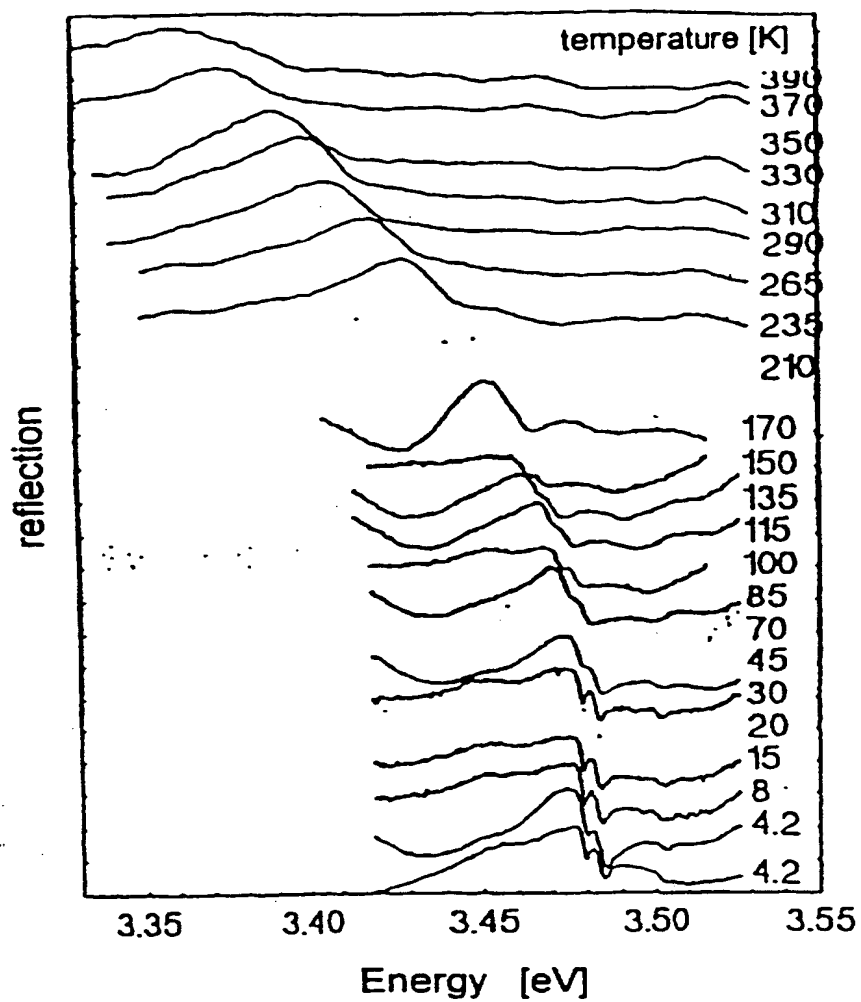


Fig 8

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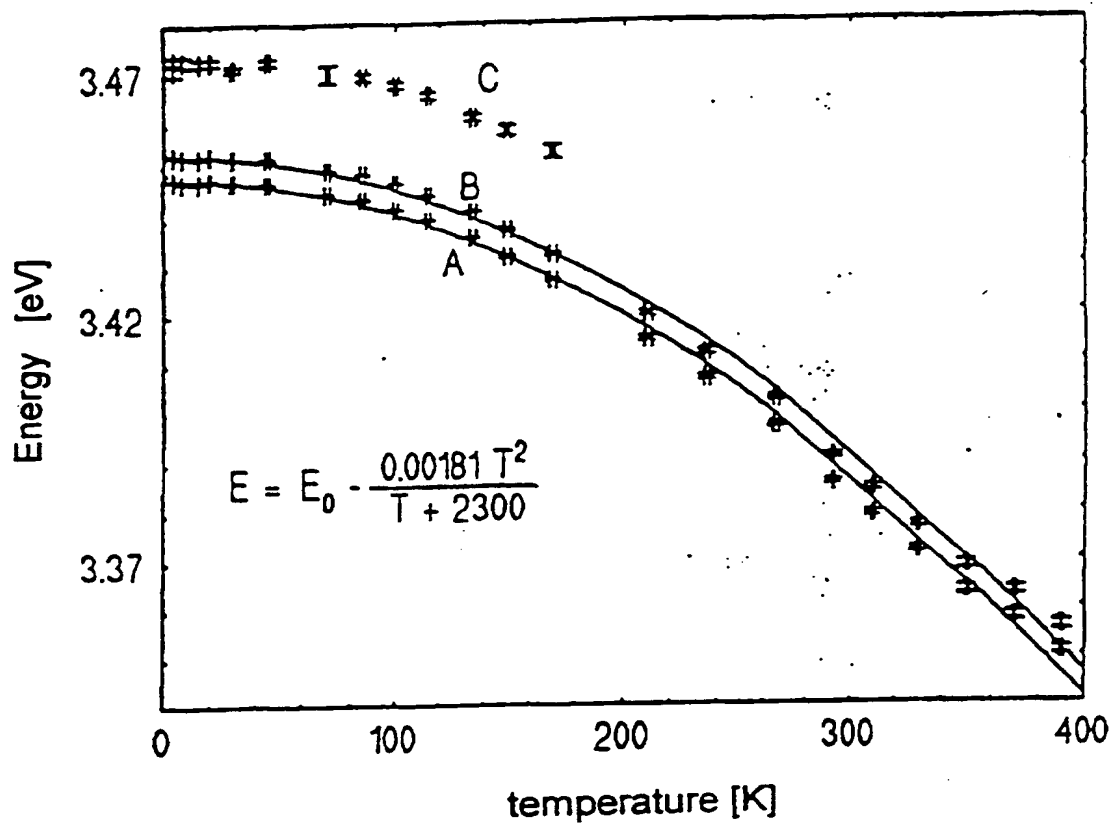


Fig 9-10

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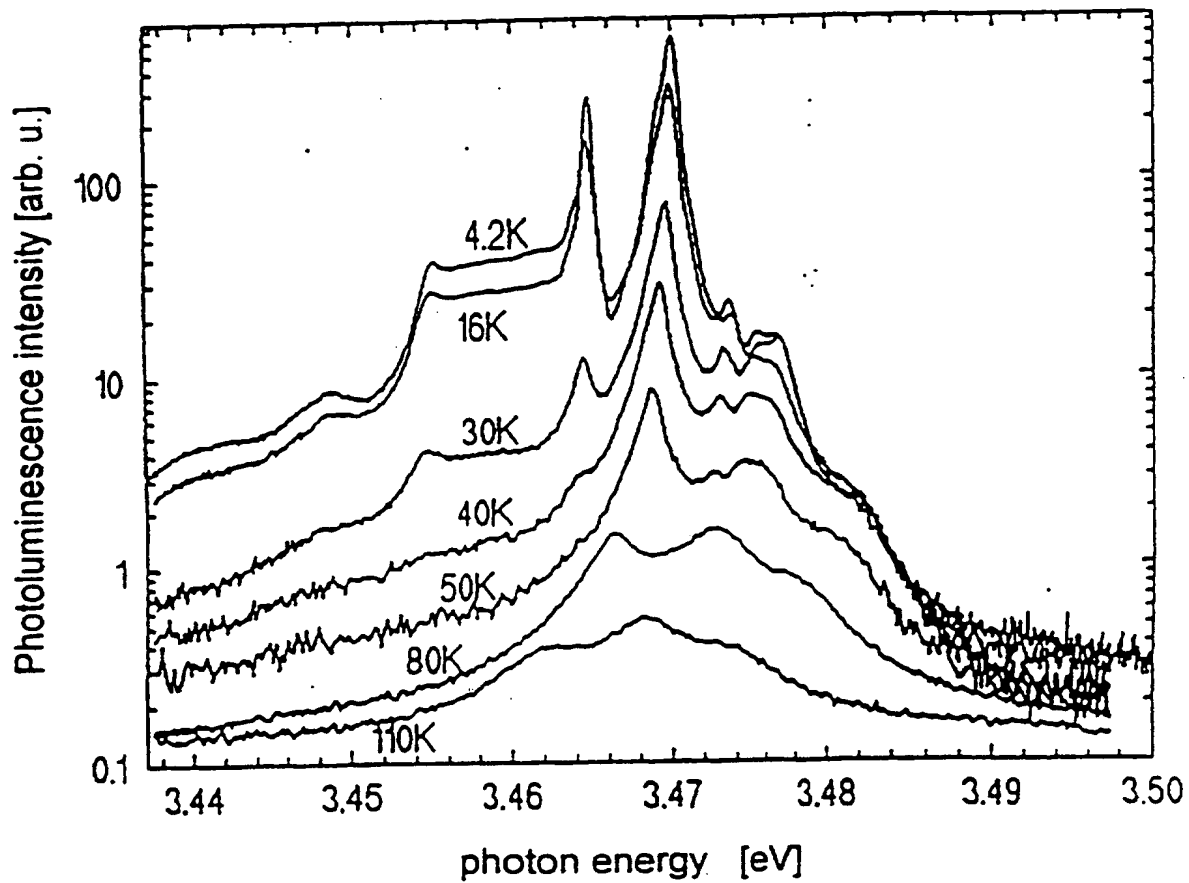


Fig 10

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# INTERNATIONAL SEARCH REPORT

International Application No  
PCT/PL 96/00017

A. CLASSIFICATION OF SUBJECT MATTER  
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## C. DOCUMENTS CONSIDERED TO BE RELEVANT

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X	WO 95 04845 A (CENTRUM BADAN WYSOKOCISNIENIOWYCH) 16 February 1995 see the whole document	1
A	FR 2 313 976 A (LABORATOIRES D'ELECTRONIQUE ET DE PHYSIQUE APPLIQUEE LEP) 7 January 1977 see claims 1-3	1
A	EP 0 371 771 A (ALCAN INTERNATIONAL LTD) 6 June 1990	

☐ Further documents are listed in the continuation of box C.

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